STUDIES OF NATURAL AND HISTORICAL ANALOGUES AND THE USE OF THEIR FINDINGS IN THE ASSESSMENT OF SAFETY BARRIER BEHAVIOR UNDER THE SAFETY DEMONSTRATION OF RADIOACTIVE WASTE DISPOSAL FACILITIES

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Article received on August 10, 2022

The article discusses and substantiates the possibility and necessity of applying the findings of studies focused on natural and historical analogues in the development of radioactive waste disposal facilities (RWDF) and demonstration of their long-term safety. It explores the issues associated with the behavior of various structural materials used in the construction of RWDF, in particular, those used in the development of engineered safety barrier system (EBS). The article overviews available publications on natural and historical analogues of engineered barrier materials — silicate glasses, native and anthropogenic copper and bronze, iron, alkaline cements, uranium deposits, as well as the system of natural reactors in Oklo considered as an analogue of deep disposal facilities for radioactive waste. It evaluates natural conditions contributing to the preservation of their insulating properties and the containment of radionuclides contained in the radioactive waste (RW) in the system of engineered and natural RWDF barriers. The study concludes that the findings of the studies can and should be used to provide parametric support in computational modeling applied to assess the long-term safety of RW disposal systems.

Keywords: *radioactive waste, natural analogues, historical analogues, radioactive waste disposal facility, engineered safety barrier materials, corrosion, leaching, safety assessment.*

Introduction

International community recognizes waste disposal as the most acceptable method that can provide adequate safety level at the final RW management stage. Safety assessment is viewed as an essential element of RW disposal projects. Moreover, the time period covered under such assessments can range from several hundred to several hundred thousand years. When repository system evolution is modeled, one of the challenges faced is seen in obtaining reliable data on engineered barrier system (EBS) materials and their parameters (or a reliable range of their values).

The concept of final RW disposal and its safety is based on the multi-barrier strategy, according to which natural barriers providing isolation shall be complemented with an EBS cascade installed to retard the flow of contaminating radionuclides. According to NP-055-14 [1], their main function is seen in restricting the contact of RW packages with natural waters and prevent the spread of

radionuclides into the bed rocks. EBS design involves primary waste form (glass-like or cement-based waste form), disposal packaging elements (container), RWDF engineered structures, buffer materials, underlying and covering caps. Figure 1 presents a general layout of a multi-barrier safety system for RW disposal.

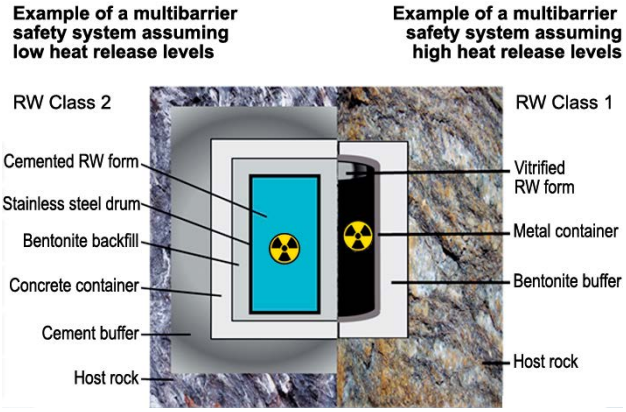


Figure 1. Layout of a multi-barrier safety system for RW disposal

It seems clear that during repository lifetime, EBS material properties may alter both due to internal processes and the processes taking place in the geological environment of the repository site during its interaction with EBS materials. These may be driven by the influence of both natural factors and the properties of the disposed waste.

Analogy method and its role in addressing the challenge of EBS system evolution and its forecasting

Each EBS system component implements the functions assigned to it. For example, a massive steel container undergoing corrosion maintains its redox potential (*Eh*). At this *Eh* level individual solid mineral radionuclide phases generally have low solubility level. Iron corrosion products may also retain many radionuclides due to their sorption and/or incorporation into the structure of secondary phases [2—5]. Clay materials used as a buffer filler provide stable pH of ground water in near-alkaline and weakly alkaline areas [6—11] and stable Eh in the reduction zone, which, together with their high sorption activity, retards the spread of radioactive substances. Materials based on Portland cement are characterized with alkaline properties retarding the transport of many radionuclides due to the low solubility of their solid mineral phases under these conditions [12]. Vitrified waste is characterized with low leaching rates, thereby limiting radionuclide release [13].

According to the regulatory framework (NP-055-14, etc.), repository evolution should be forecasted based on numerical models, but the extent to which they can be verified via traditional approaches is essentially limited due to the short research time compared to the repository lifetime. Therefore, the key challenging points can be summarized as follows:

- the way the EBS materials used in the engineering protection behave themselves during the period under consideration (up to millions of years);
- the *upscaling* problem, i. e., upscaling laboratory and point-source data to an industrial facility, which cannot be addressed directly under laboratory conditions.

Due to the complexity of the processes occurring in repositories, these practically cannot be comprehensively recreated under laboratory conditions. Moreover, one should consider those processes that are influenced by natural inhomogeneities involving large uncertainties and having a very long-term impact. In this case, laboratory data shall be supplemented with information from *in situ* URL experiments and analogue studies, including natural and historical (anthropogenic) ones. In this respect, analogues seen as systems the properties of which are similar to RWDF components play rather a unique role. Many archaeological materials have preserved in conditions considered more aggressive or dynamic than those expected in the repository. Analogues can be rather conventionally divided into natural and historical ones. Natural conditions are thought as conditions, materials and processes of natural origin, similar to or resembling those occurring or applied in the construction and operation of RW disposal facilities. Whereas, historical analogues are the materials, structures and buildings created by man. The difference between these categories is quite conventional since both natural and historical facilities operate in the conditions of their interaction and mutual influence. Potential application of this approach once again confirms the multidisciplinary nature of the RW disposal challenge. Geological and archaeological studies, application of relevant methods and findings increase the reliability and validity of modeling forecasts regarding disposal system evolution, which, in turn, increases the reliability of long-term forecasts under the safety assessments. Historical analogues are believed to be most applicable in case of near-surface repositories (NSDF) designed for low-level waste disposal, where the waste activity is mainly influenced by short-lived radionuclides. In this case, radioactive substances shall be reliably contained within the repository for no more than 300—1,000 years, which corresponds to the period

of reliable historical knowledge available to the mankind. Such analogues can be considered both to study the behavior of various materials applied in near-surface repository construction, including the process of EBS design development, and under the siting process with an account taken of relevant natural and climatic conditions.

Considered below is the applicability of the analogue method in the long-term predictions focused on the characteristics of some materials that are most often used in the construction of disposal facilities and EBS.

Study of analogues

Analogues may be studied in many ways with the focus placed on relevant natural systems as long as such research provides any quantitative or qualitative information that can be used in the safety assessment of a repository system. Basically, such analogues may provide quite valuable support under any safety assessment.

Another point to note is that material composition of RW container may differ from the one of historical artifacts. Therefore, for example, silicon carbide, stainless steel, nickel- and titanium-based alloys have been developed relatively recently and cannot be considered completely analogous to the historical artifacts. Correspondingly, among such artifacts one may search the information only regarding the materials with similar chemical composition — carbon steel, copper and some alloys, some types of glasses and cements.

Table 1 summarizes the application of natural and historical analogues in the study of multi-barrier safety components.

Table 1. Application of natural and historical analogues in the study of multibarrier safety components

Multibarrier safety system element	Analogues
EBS materials in the near field	
Matrix waste form	Natural and technogenic glasses seen as analogues of vitrified high-level waste
Clay-based buffer material	Natural analogues
Metals	Natural and technogenic materials
Materials based on Portland cement	Natural and technogenic materials

Analogy between RWDF and uranium deposits

In their essence, deposits of radioactive elements are in many respects similar to deep disposal facilities. Deposits of both radioactive and stable elements and their study help to identify the basic principles for the selection of adequate geological conditions for the repository sites [14—16]. Analogy with ancient uranium deposits is usually used as an argument supporting the decision-making on potential development of a safe DGR. From this perspective, of particular interest is the uranium mine Cigar Lake (Canada) (Figure 2) in cemented sandstones reaching a depth of 430 m from the surface. The lens-shaped ore bodies were formed approximately $1.3 \cdot 10^9$ years ago [17]. This is a quite high-grade uranium deposit (up to >40 wt.%) accommodating some significant uranium reserves (estimated amount accounts for 150 thousand tons, which is comparable to the amount of SNF in a DGR). First of all, this deposit is remarkable since there are no surface indications of radioactive ores occurring at a depth, which is much of interest considering the safety requirements. The analogy between a DGR and the Cigar Lake deposit seems

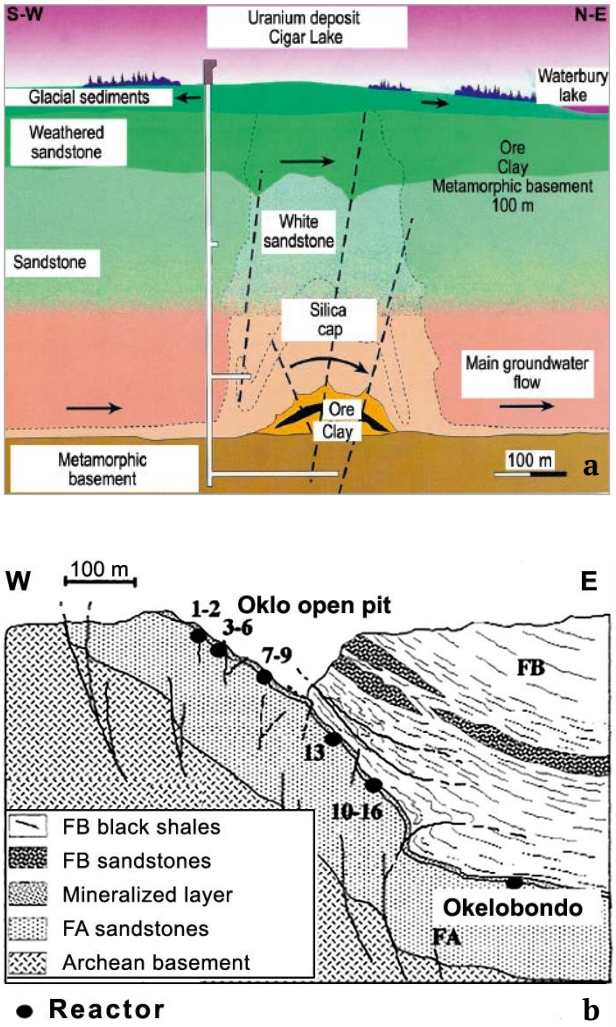


Figure 2. a) Schematic section of the Cigar Lake deposit, rock types, main tectonic faults (dotted line) and the direction of the modern groundwater flow [17] (quoted from [18, 19]). b) Geological structure of the Oklo reactors [23]

quite remarkable, firstly, since in the context of the disposal safety, the case study of a natural uranium deposit demonstrates how important is the knowledge about the transport of artificial radionuclides in a natural environment.

In terms of radionuclide transport, the Oklo uranium ore deposit (Gabon) and the neighboring deposits are considered quite interesting case studies. Approximately 1.7 billion years ago, nuclear fission reactions proceeded in this area for at least 0.5 million years [20]. This case study is considered especially important due to unusually high-level enrichment of original rocks with uranium: at the time of its formation, the ores contained from 50 to 70 % of uranium oxide, the share of ^{235}U in which was about 3 %, which corresponded to the one of nuclear fuel from fission reactors. Periodic flooding has contributed to chain reactions that took place in some parts of the deposits: the subsoil has heated to 900 K causing water evaporation and attenuation of the chain reaction until next flooding. The process occurred periodically until fissile isotope inventory got exhausted. Mobile radionuclides moved away beyond the natural reactor area, but the ancient age of the deposit cannot provide any reasonable conclusions on the conditions that could cause this transport [21, 22]. Figure 2b presents the geological structure of the Oklo reactors [23].

Specific aspects related to the interaction of natural uraninite with the geological environment were explored based on the case study of uranium ores from the Streltsovsk ore field [14, 24]. The evaluated mineral composition of the ores showed that the primary uraninite, $UO_{2-2.677}$, had been interacting with post-mineral thermal solutions, which resulted in a secondary uranium-silicon gel that replaced the primary mineral exclusively within the ore bodies. No noticeable uranium release did occur beyond its boundaries indicating uranium inactiveness under reducing conditions.

The above noted facts about the nature of natural processes occurring in deposits of natural radioactive elements are considered also true for RWDF. Thus, in general, the main characteristics of uranium ore bodies that may be relevant as analogues can be summarized as follows [16]:

- composition, long-term stability and behavior of uraninite as an analogue of spent fuel, corrosion/dissolution (although it should be bared in mind that there are some fundamental differences between natural uraninite and SNF, the most important of which is that the former, except for natural reactors, has not been exposed to criticality, therefore, it did not contain significant concentrations of fission products, internal irradiation from the decay of which could cause significant damage to the structure of the material);
- the role of redox processes in radionuclide mobilization and retardation, including redox fronts and other geochemical heterogeneities, as analogues of conditions formed around RW container;
- composition and solubility of radionuclides in groundwater (including colloid formation) as an analogue of their behavior in EBS and host rock;
- processes associated with radionuclide transport in groundwater affecting remobilized substances, including sorption phenomena on various surfaces, generation of solid mineral phases and diffusion into the rock matrix, as an analogue of radionuclide behavior in RWDF;
- potential applicability of disequilibrium between some natural decays to assess the durability of various transport and deposition processes as an analogue of the processes expected to occur in the EBS and the geological environment.

Analogues of EBS materials

Natural and anthropogenic glasses as radioactive waste form analogues

Back in the 1950s, glasses were proposed as possible RW form. Basically, two glass compositions are currently used for RW vitrification purposes — borosilicate (UK, France, USA, Russia) and aluminophosphate glass (Russia). Volcanic glasses can be considered as natural analogues of such glasses. Their age ranges from 2 to 20 million years. Volcanic glasses up to 40,000,0000 years old have been reported [25]. Natural volcanic glasses have a SiO_2 content similar to the borosilicate ones (used for HLW vitrification purposes). Nevertheless, they have low concentrations of both boron and radionuclides. Two main types of glass are considered most closely: those with a high silica content (rhyolite glasses and tektites) and those with a low silica content [25]. The earliest archaeological anthropogenic glasses date back to 4,500 years and were subsequently produced using a wide range of compositions, usually from soda-lime or potash-lime mixtures [24]. Many archaeological artifacts have survived essentially unchanged for 3,500 years [26].

Studies have shown that the leaching mechanisms are similar both in case of natural and borosilicate glasses. It has been demonstrated that devitrification (recrystallization in the solid state) proceeds at a quite slow rate and, therefore, should not be considered a serious problem for RW [27]. Under general glass dissolution mechanism, both parallel and sequential reactions occur [28, 29]. In nature, glass dissolution and hydration results in layers of secondary alteration products that slow

down further processes and may also involve some leachable radionuclides [30]. Volcanic glasses are usually sampled by researchers from near-surface or underwater aerobic environments. For this reason, although being different from the anaerobic deep disposal conditions, they can provide important information about borosilicate glass behavior.

Some studies were also focused on archaeological evidences. In particular, a ship that sunk some 1,800 years ago was found in the Mediterranean Sea at a depth of 56 m. A plate of Roman soda-lime-silicate glass was found on it (its composition was as follows, wt%: 70 — SiO_2, 20 — Na_2O, 5 — CaO, 1.8 — Al_2O_3, 3.2 — other elements) [31—34] (Figure 3a). Throughout the time, it interacted with sea water at a temperature of about 15 °C. Cracks formed during melt quenching were found in the glass samples. Maximum thickness of the altered zone amounted to up to 500 μm and was observed near the surface, whereas, along the cracks away from the surface, it did not exceed 5 μm. Based on a reference archaeological glass block, the authors of the study [34] showed that the surface area formed by the cracks was 86 ± 27 times greater than the geometric one, but the volume change accounted for only 12.2 ± 4.1 %. Microcracks in glass were found to be filled with smectite.

In literature sources, volcanic glass is often considered as a natural analogue of borosilicate glasses. One can note a similarity in their transformation mechanisms: the effect of aqueous solutions on natural glasses is limited to the replacement of ions of alkaline and alkaline earth elements by hydrogen ions, glass hydration, its partial dissolution and precipitation of secondary phases [35]. The leaching rate both in case of volcanic and borosilicate glasses usually decreases with time by three to five orders of magnitude. However, this is not always the case: a case in point is a study [36] drawing analogy between volcanic and borosilicate glasses with some particular focus placed on the mechanisms governing glass dissolution under silica saturation conditions. A series of laboratory experiments was performed involving synthetic glass of natural composition at 90 °C and a pH level of 7 in saturated aqueous solution for more than 600 days. The authors of the study [36] revealed its corrosion with an unexpectedly high and constant dissolution rate of $4 \cdot 10^{-3}$ g/m²·day, which was explained by the absence of near-surface gel passivation. The thickness of the palagonite layer formed over 1,000 years ranged from $3 \cdot 10^{-4}$ to 50 μm.

Corrosion rates of $1 \cdot 10^{-3}$ μm per 1,000 years have been noted for glasses older than 1 million years, however, no direct relationship between the age and the layer thickness has been established. An experimental study of natural glasses showed that they can be considered as a reliable analogue in the long-term assessments of vitrified RW properties [37].

Dissolution rate of both borosilicate and aluminophosphate glass in a closed medium is known to be characterized by very low values, usually several orders of magnitude lower than the initial dissolution rate [38, 39]. Usually, the corrosion rate of volcanic glasses varies from 0.1 to $n \cdot 10^1$ μm per 1,000 years. The low glass transformation rate indicates that vitrified RW under similar conditions can retain their containment properties for a long time.

Quite remarkable are the studies of uranium-containing glasses, which have been implemented since early 1800s [40]. [31] describes items based on it produced in the Czech Republic. Glasses containing uranium (about 5 wt.% uranium in some samples) can provide useful information about uranium leaching and incorporation into secondary products. In total, about 20 kg of glassware being about 80 years old were recovered from an old partially flooded waste dump. Corrosion of uranium glass samples was found to be uniform with an altered layer being 100–500 μm thick, having a sharp interface with the unaltered glass and no transition zone; the corrosion rate was found to be ranging from 1.25 to 6.25 μm/year. Measurements showed approximately tenfold enrichment of uranium in the surface layer (0.5 μm) compared to the glass matrix (found in two samples). Figure 3b demonstrates the appearance of an item made of uranium-containing glass containing uranium in UV light.

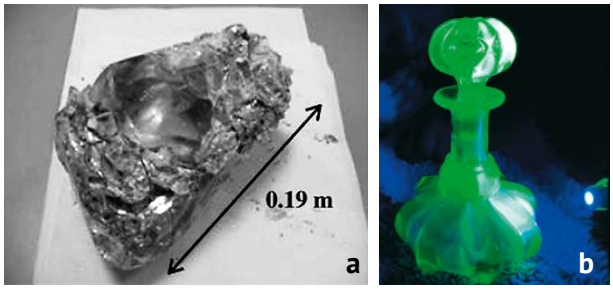


Figure 3. a) Appearance of a Roman glass block [34]
b) item made of uranium glass in UV light [41]

Bioactivity in the presence of organic matter seems to accelerate the dissolution of glasses [31]. The outer part of the altered layers had a thickness of about 10—20 μm, increased towards the center of the samples and decreased towards their periphery. Organic matter in the samples was mainly concentrated in the outer parts of the surface layer. The composition of several structurally complex surface layers with a thickness of 10 to 100 μm showed that

larger cations (Na, Ca and partially Si) have leached, while Al got accumulated in the degraded surface layer, which was considered typical in case of silicate and aluminosilicate weathering. In the outer surface layers, crystalline phases were identified, which appeared to be layered aluminum silicates of the 2 : 1 structural type (hydromica, montmorillonite and calcium-containing zeolite). Biological activity was stimulated by organic matter causing acidification of the resulting carbon dioxide and higher aggressiveness of the medium to the glass material. Thus, more detailed studies shall be implemented to explore the impact produced by organic substances (including biogenic processes) on the rate of silicate glass alteration/destruction, as well as other barrier materials (in light of the above, programs are being developed to study the microbiological effect on the processes occurring in the near field [42—48]).

Unfortunately, neither artificial nor natural analogues of aluminophosphate glasses exist.

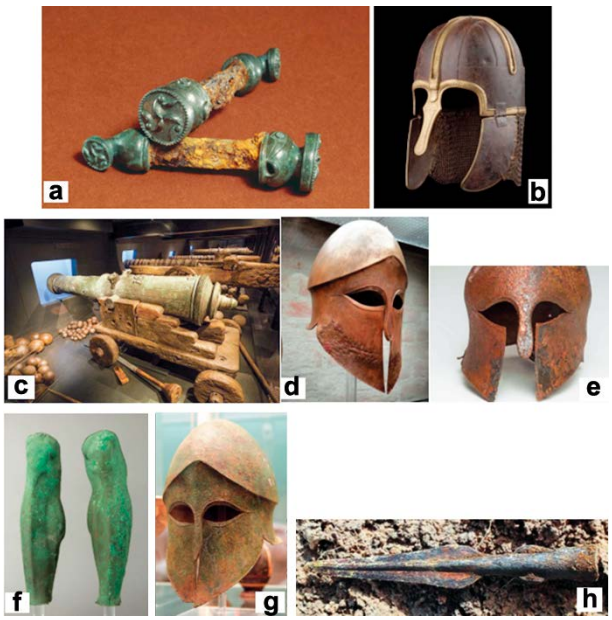
Studied analogues of metal EBS elements

Similar to the glasses, the role of analogues and their study is believed extremely important to provide reliable forecasts of container material stability. Laboratory experiments last for years, at best up to 10 years, while the behavior of this EBS element must be predicted correctly for a much longer period. Thus, in archeology, there are well-documented evidences demonstrating the stability of anthropogenic metal materials for hundreds of years (for example, elements of the Papal Palace in Avignon have been quite stable for over 650 years).

Copper and copper-based alloys

Natural copper nuggets from the Permian-era Littleham Mudstone Formation (Littleham Cove, south Devon, southwest England) have been studied as analogues to demonstrate the long-term stability of a copper container installed into a bentonite buffer [49]. Copper content in them amounts to 99.9 %. These are plates being up to 160 mm in their diameter and up to 4 mm thick. These nuggets are immediately associated with uranium-vanadium-bearing nodules and areas of red mudstone reduction. A study [49] showed that in a compacted clay environment, metallic copper could remain stable and resist corrosion for a very long time period. In this case, copper was literally isolated in a matrix of naturally compacted mudstone for at least 170 million years (such periods were much longer than the time frames considered in the safety assessment of RW disposal facilities focused on copper containers — up to 10^6 years), until uplift and erosion caused its release into the weathering zone, where it has corroded. The natural clay formation of Littleham Mudstone was not highly compacted, unlike the bentonite clay used in the EBS DGR system. Therefore, preservation of metallic copper in this natural environment evidences that copper containers may resist corrosion well.

Excavations at Kirkburn site in East Yorkshire (England) testify that household items corrode with no evidence of extensive damage to the bronze caps at the tail-ends of iron studs [50] (Figure 4a). Another interesting item found in clay soils is the Coppergate helmet (Figure 4b). It was discovered in May 1982 in a swampy pit at the Coppergate excavation site, York, UK [52] (as estimated, it was manufactured around 750 AD). Its inner part was filled with dense clay. Microbial activity was estimated as low. The environment was anaerobic (similar to the expected DGR conditions), which provided excellent preservation of the hamlet. No crust made of corrosion products was found on the hamlet parts covered with brass-based material or in the spots where the plates were riveted and covered with other metal layers. The brass material was susceptible to corrosion degradation that resulted in the generation of chalcopyrite ($CuFeS_2$) and bomite (Cu_5FeS_4). The degradation level ranged from light



a) Lock pins of a chariot [51];
b) Coppergate helmet, Yorkshire Museum [53];
c) Bronze cannon from the Mary Rose warship [55];
d) Bronze Corinthian helmet found in the tomb of Denda, from a Greek workshop in southern Italy, 500-490 BC;
e) A helmet discovered at the bottom of the Mediterranean Sea in 2007;
f) Greaves of the V century BC;
g) Bronze helmet of the Corinthian type, around 500 BC, British Museum [58];
h) Bronze spearhead, Gloucestershire, England [59]

Figure 4. Appearance of corroded copper and bronze artifacts

surface coating with a black corrosion layer to damage spots.

In July 1545, the Mary Rose warship sank near the Solent, west of Portsmouth, England [54]. Its wreck was recovered from the water after 437 years. A few metal artifacts were discovered (chain dredgers, cannonballs, cannons, dishes, coins, etc.), including those made of copper. Under anaerobic conditions prevailing at the bottom, none of these items was found to be intensely affected by corrosion (Figure 4c).

Samples of Chinese bronze from archaeological sites discovered in subtropical humid regions, were found to be covered with corrosion crusts being 320—800 μm thick, in contrast to 50—260 μm thick layer typical for samples found in a drier temperate climatic zone. The maximum corrosion rate was estimated at about 7.27 μm/year [56, 57].

In case of Argentinean bronzes, the corrosion rates were found to be varying in a wide range [31]. Five artifacts corroded at a rate ranging from 0.08 to 0.17 μm/year, which corresponded to the range indicated in the review [57]. No pitting was observed on any of the bronze specimens, only areal corrosion was present. However, the surviving ancient Greek bronze armor was specifically characterized by predominantly local corrosion: many helmets have preserved quite well. Nevertheless, most of them had local corrosion spots: small dots and holes (Figure 4d—4g).

A study exploring bronze samples being 2,100—2,400 years old [31] showed that relevant corrosion rates were distributed in the same range as in other copper-based materials: maximum levels were somewhat higher than those given in the review [57]. At the same time, high tin bronzes were characterized with the lowest corrosion rates, which were about an order of magnitude lower than the atmospheric corrosion rates typical for tin modern bronzes. Nevertheless, they were susceptible to brittle mechanical degradation. This effect requires further study.

An almost intact Bronze Age spearhead was found at Cirencester, Gloucestershire, England [59] (Figure 4h). Spearhead age was estimated as being over 3,000 years old. It was discovered at a depth of about a meter.

Alkaline soils with higher organic matter, sulfur and chlorine content and an increased pH level were found to be more aggressive towards copper and its alloys [31]. The studied corroded samples revealed an outer mineralization layer consisting of cuprite, malachite and covellite, as well as Cl, C, Fe and Al from the surrounding soils. Cast specimens had larger and less uniform grain sizes compared to thermally and mechanically treated rough forges and were susceptible to grain boundary corrosion. The cast copper artifact had higher corrosion rate, close to the upper limit of the range reported in [57], which seemed to indicate that mechanical treatment could increase corrosion resistance providing compaction of the surface layer.

Quite extensive data review focused on the corrosion rates [57] of bronze-copper artifacts from various media states the following range for copper and copper alloys - up to 0.025–1.27 μm/year (on average, about 0.3 μm/year). According to [56], the average corrosion rate of bronze and copper artifacts was estimated at 0.23 μm/year, while tin bronzes were found to be a more corrosion-resistant material. [60] indicates that in case of archaeological artifacts preserved under anaerobic conditions this indicator varies from 0.05 to 4 μm/year. This is true for most soils under slightly or moderately aggressive conditions considering an exposure time of less than 20 years and assuming further decreasing rate, while the patina layer thickness ranged from 10 to 250 μm. Meanwhile under aerobic conditions the rate amounted to 36 μm/year.

Pitting corrosion of copper and bronze artifacts was studied: the average pitting factor (the ratio between the depth of the deepest pitting driven by corrosion process and the average penetration calculated based on mass loss) of about three was identified [31].

Iron and steel

Due to chemical properties of this material, data on iron corrosion can be mostly obtained from available historical analogues. In addition, such analogues are considered of interest when it comes to carbon steel and its applications, especially given the impact produced by anaerobic corrosion products on the stresses in the neighboring materials due to the increase in their volume. Given relatively low anaerobic corrosion rate typical for cast iron and carbon steel (up to a few microns per year as shown below) and the long timeframes considered for the geological disposal of containers with RW, a few studies have been carried out to explore the corrosion of iron samples that have been exposed to anaerobic conditions for quite a long time. Archaeological artifacts (a time period of over 1,000 years), as well as materials of modern industrial and domestic structures (a time period of less than 1,000 years) were considered as such historical analogues.

The case study of the Sainte-Gervais church in Paris (Figure 5) has revealed a picture being quite similar to the DGR conditions as regards pH, *Eh* levels and the solution composition. Four areas could be distinguished on the iron items: metal; dense

layer of corrosion products; intermediate region of iron diffusion into the cement sheath and cement masonry [61]. Archaeological finds provide information on the overall degradation rate and manifestations of local corrosion in them. The degradation rate estimated for iron-based materials based on these studies was found to be ranging from 2 to 20 mm over 10^4 years [62].

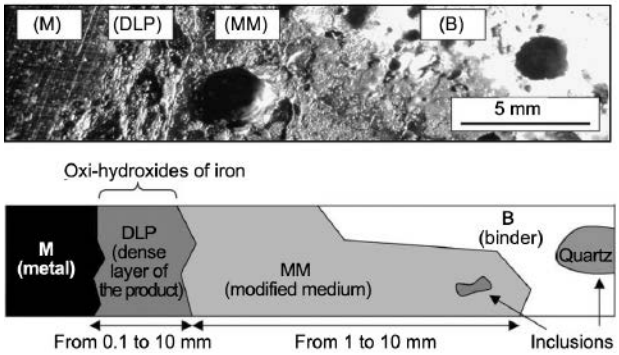


Figure 5. Macrophoto of a cross section (Saint-Gervais Cathedral — Church of Saints Gervasius and Protasius) and a schematic section of steel reinforcement corroded in an ancient binder (M — metal; DLP — dense layer of the product; MM — modified medium (modified layer); B — binder) [61]

As mentioned above, the Coppergate helmet also contained iron parts. The dome consisted of eight individual iron plates riveted together. Their thickness ranged from 0.7 to 3 mm [52]. Well-preserved iron mail-armour around the neck made of wire with a diameter of 0.9—1.2 mm. The corrosion degree varied from a light surface coating with a black corrosion layer to damage spots. The dense black spot was identified as siderite ($FeCO_3$). The corrosion product of iron fragments appeared to be not magnetite (Fe_3O_4), but siderite ($FeCO_3$).

Considering relatively low anaerobic corrosion of cast iron and carbon steel [16, 63—66] and the long timeframes provided for in the RW containers under geological disposal designs, a few studies implemented in the field of RW disposal were specifically focused on the corrosion of materials that have been for a long time isolated in different environments. There are several examples of native iron samples found in geological facilities with reducing potential and high pH level [67].

Such analogues could evidence whether under anoxic conditions, corrosion products formed on ferrous metals could cause such high-level stress in a confined space that would be enough to deform the surrounding material. Relevant findings could be compared with those of experimental studies focused on the mechanical properties of oxides and the expansion caused by corrosion [68]. In air, ferrous ions are oxidized to FeOOH causing volumetric expansion and cracking of the corrosion product film. Iron nails dating back to the 19th century from residential buildings in the United States were studied. The findings reported in [70] demonstrated that an impermeable surface layer of Fe_2O_3 formed during a house fire protected them from further corrosion. Among the corrosion products, both iron oxyhydroxides [69—76] and sulfites, sulfates and sulfides [64, 65, 72, 73], as well as carbonates [74] were found. It should be also noted that sulfate reducing bacteria cause the development of sulfide films on the surface [64, 65].

[57] presents corrosion rate calculated for archaeological iron artifacts. Under anaerobic conditions, the rate was estimated at about 0.1 μm/year, which is consistent with long-term laboratory experiments involving steel wire immersed into oxygen-free artificial groundwater [66] (see below). In [74, 78], archeological artifacts were subject to electrochemical measurements. Most wrecks and artefacts exposed to oxygenated seawater corroded at a rate of 100—200 μm per year (a level close to currently predicted corrosion of carbon steels in seawater [79]). [76] focused on the magnetite corrosion product found on the surface of cast iron that has been interacting with clay soil in a coal mine for 60—90 years: a corrosion rate of 1—10 μm/year was calculated based on their thickness. According to an extensive review of data focused on the corrosion rate [57] in various media, the uniform corrosion rate of iron and its alloys was limited to 0.1—10 μm/year suggesting that a massive iron container can last about 100,000 years (as calculated in [80]). Nevertheless, iron artifacts give little or no information about pitting, which may greatly shorten this period.

Literature sources show that certain traces of local microbial activity have been revealed for corrosion products formed at archaeological sites. However, some parallels can be drawn between the corrosion of archaeological items and the likely behavior of an iron container. The good preservation of the Coppergate helmet and Iron Age artifacts at the Kirkburn site — nails and many other artifacts — evidence that under anaerobic conditions iron and, hence, carbon steels corrode at a very low rate. Therefore, materials based on carbon steels can be considered promising for their further use in EBS systems.

Industrial analogues

In modern industry, there are a few facilities in which water is present under conditions corresponding to the reducing DGR environment being in contact with iron [81]. Such facilities involve:

- plumbing and heating systems, in which copper pipes and steel radiators are exposed to water and

magnetite usually gets deposited in the heating systems;
- pipelines represented by reinforced concrete structures on the seabed, in which the diffusion rate of oxygen through the concrete appears to be low, thus, anaerobic conditions prevail at the reinforcement surface.

Particular attention is paid to the phenomenon of the so-called oxide jack, which is caused by an expanding force due to volume increase during corrosion product formation: their density appears to be lower than the one of iron and carbon steel. This phenomenon is observed in building structures (railings around St. Paul's Cathedral and the Acropolis in Greece [82]), in heat exchangers at nuclear power plants [82] and in case of atmospheric corrosion causing cracks in the surrounding materials (for example, copper [83, 94]).

Studies of natural analogues focused on cements and high pH water systems

Archaeological records provide numerous examples of cement and concrete compositions. Until the beginning of the XIX century, lime-based cements were mainly used, whereas the Romans applied pozzolanic materials. Modern Portland cement has been in use for over 150 years and is a cement type being widely applied in repository construction. Water interaction with cementing zones results in high pH solutions able to react with wall rocks and barrier clay material [84, 85]. Natural systems with high alkalinity can be similar to the pore water in cements and concretes applied as building material in RW repositories. Such alkaline systems and relevant studies provide information on the solubility and forms of radionuclides at high pH levels that can be analogous to pore water flows from the repository to the host rock and microbial processes occurring at high pH levels. [86] focuses on Gallo-Roman cements older than 1,500 years. Calcium silicate hydrate (CSH) compounds were formed during the early development of Roman cements: these cements involved pulverized glass-like chamotte clay in the concrete mix. The Hadrian's Wall cement material in England, which is about 1,700 years old (its appearance is shown in Figure 6) involves the same calcium silicate hydrate phases as modern Portland cement and is still characterized with adequate strength and stability levels. Moreover, [86] indicates that, as long as there is no serious physical damage, cements remain quite stable. Similar results were obtained in the study of early reinforced concrete structures in the UK and the very first Portland cements used in the defense of the England coast since the second half of the XIX century [87].

Figure 6. Hadrian's Wall in Birdoswald being about 1,700 years old [88]

The data show that the processes occurring in the DGR will mainly affect the near field of the barriers and practically will not spread across the geological barrier [89]. Metacarbonates of sandinite facies (e. g., Christmas Mountains aureole and Marble Canyon, Texas) may be considered as natural analogues for high silica cements that can be applied in EBS construction. They are potentially considered as quite valuable alternatives to high silica cements for two reasons:
- many of the phases occurring in them are exact analogues of the phases found in cements with high silica content (most types of modern Portland cements);
- since they have been exposed to atmospheric weathering factors for sufficiently long time periods in different environments, these can be used to predict the preservation ability of cements with high silica content under repository conditions over different time periods.

Observations show that the cement material can be considered reliable and durable, for example, the age of the oldest cements in Maqarin in northern Jordan amounts to about 2 million years [90]. Considering this analogy, groundwater pH level (up to 12.9) depends on the solubility of natural cement phases. Alkaline groundwater in Makarin interacts with host marls causing the dissolution of some aluminosilicates and the precipitation of some secondary calcium-silicate-hydrate compounds and zeolites. These reactions have been observed and used in the development of conceptual models presenting interactions between reservoir leachate plumes and far-field rock [91]. A project titled Natural Analogue of Maqarin was focused on the evolution and conservation of highly alkaline groundwater in this area as a product leaching from these natural cement minerals [92].

[93] reported the presence of unreacted natural cements at the Scout Hill and Carneal Plug sites in

Northern Ireland. Their estimated age is about 58 million years. Under these case studies, the natural cements were considered as virtually impermeable and remained intact until groundwater inflow did occur. A tendency was identified: the pores of the system tended to re-sealing either with secondary phases of $CaO—SiO_2—H_2O$ (CSH) or carbonates following carbonization reactions.

[94] evaluated cement leaching from a cement water tank built in Sweden more than 90 years ago. Calcium depletion in a 8 mm-deep water-contact layer was revealed during the study, whereas silica mainly remained an immobile element and the content of potassium and sodium increased in the carbonization zone. Some mineralogical transformations were observed in the cement: old clinker phases tended to dissolve with some calcium and sulfate-containing phases generated, such as portlandite, ettringite and thaumasite. In the spaces after the former clinker grains, secondary calcium silicate hydrates (C—S—H phases) with a CaO/SiO_2 ratio of about 1 : 1 were observed. Carbonization resulted in calcite formation, which, together with manganese carbonate also formed a crust at the level of the open water surface. This zone had lower porosity.

Natural cements from Jordan are considered as natural analogues of modern industrially produced alkaline Portland cements traditionally applied in repository construction [92, 95]. These cements were formed due to high-temperature metamorphism of bituminous marls and limestone caused by spontaneous combustion. A slightly alkaline cement analogue from Oman was studied in [96]. The study was aimed at testing chemical thermodynamic models used in the safety assessment of RW disposal facilities implying their "blind" application to a natural system similar in its chemical composition.

[97] studied the samples taken from a well filled with concrete (as concrete-clay interaction analogue) based on a core sampled at the Tournemire site, France. It helped to simulate radioactive substance transport taking into account thermodynamics and kinetics using the HYTEC code and given a 15-year timeframe. At 15 °C, the secondary mineral sequence modeled from concrete to mudstone provided for the following succession: CSH/ettringite/carbonates at the concrete/argillite interface followed by a neoformation zone of clay-like phases and calcite, and the last one involving calcite depositions. The calculations also provide correct forecasts regarding carbonate formation at the concrete/mudstone interface.

Based on the above examples of natural cement studies, one may conclude that historical and natural analogues of high-alkaline cements may serve a useful tool in forecasting the behavior of the developed RW repositories with alkaline cements proposed in their designs.

Bentonite buffer and study of its natural analogues

Under numerous repository designs, bentonite clays are most commonly proposed as barrier materials, which is explained by their specific properties, such as plasticity, swelling capacity, high sorption activity, low hydraulic permeability and diffusion coefficients, stability in geological environments. However, bentonite appears to be unstable at high pH levels, which reveals a problem, namely, when concrete building material interact with alkaline leachates [98].

[99] notes that the Mangatarem site in the Philippines, where a bentonite and zeolite pit was discovered in the sedimentary shell of the Zambales ophiolite, can be considered promising to study the interaction of bentonite/hyperalkaline solutions and its application as a natural analogue, since hyperalkaline underground waters of ophiolite origin (pH 10—11) were found in the immediate vicinity of the pit.

[100] explores potential bentonite behavior when exposed to natural groundwater with high pH level (10—12) originating from the ophiolites of the Troodos belt in Cyprus as an analogue for a reaction between EBS bentonite and leaching products from low alkaline cements. It was found that over a period of 10^5—10^6 years, the alkaline reaction occurring between groundwater and bentonite was quite negligible, indicating that any long-term reaction between EBS bentonite in a storage facility and low alkaline cement leachates would be minimal. Such a setting seems quite similar to the one expected under repository conditions:

- sufficiently large mass of bentonite (hundreds of tons) reacts with leaching products;
- the corresponding alkaline leachate can react with the bentonite surface;
- reaction time scale (hundreds of thousands to millions of years) is much more relevant for RWDF than accelerated laboratory experiments and studies in URL conditions (lasting for several months or several years).

Discussion

Figure 7 provides visual representation of corrosion rates for the materials of natural and historical analogues, in particular, glasses, iron and carbon steels, copper and alloys under aerobic and anaerobic conditions. The corrosion rates for the analogues were set forth based on the available information,

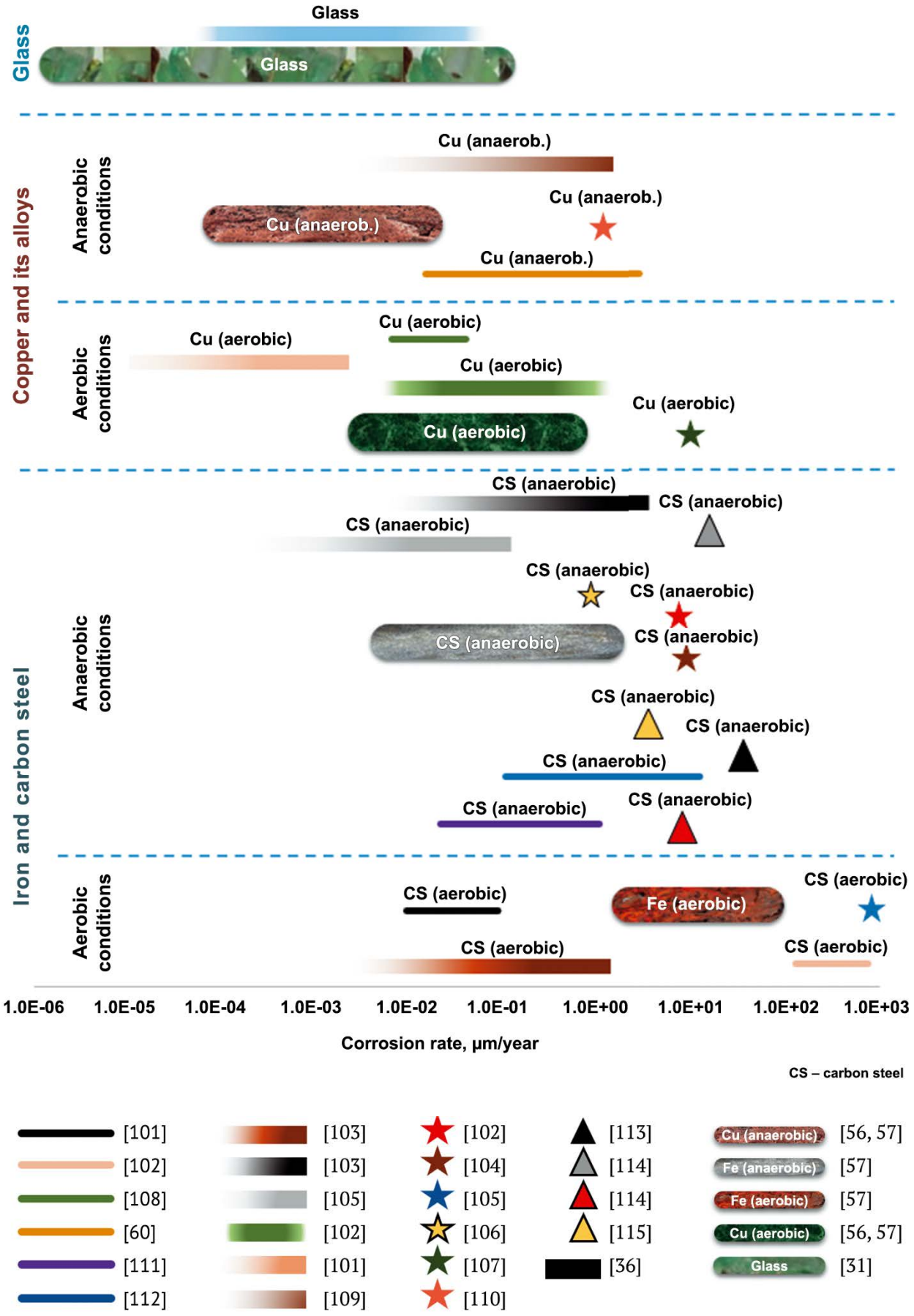


Figure 7. Materials of natural analogues and visual representation on their corrosion rates (μm/year) given in various literature sources (indicated in brackets). Ranges of values are shown as segments

according to [36, 38] for volcanic glasses, [31] for uranium-containing glasses, [56, 57] for copper, [57, 76] for iron and carbon steel. Since short-term experiments (lasting for years) implemented under numerous experimental studies to study copper corrosion rates, as well as the those of carbon steel and iron provided a huge array of information, these data were also presented for comparison purposes. Another remarkable aspect is that the average corrosion rate for metals and alloys estimated based on short-term experiments usually turns out to be similar to the one of analogues. Another point to note is that the presence of oxygen accelerates metal corrosion.

Copper appears to be a quite stable material. One can note clearly that its corrosion rates calculated based on analogue studies are commonly somewhat lower than those obtained from short-term experimental studies. This is also true in case of iron corrosion under anaerobic conditions. Copper and iron corrosion data can be applied in the forecasts of EBS material behavior. Table 2 summarizes the findings of research focused on natural and historical analogues of materials used in the EBS construction. Due to the different chemical composition of natural and archaeological glasses and no radiation impact involved, it appears quite risky to use them as analogues when it comes to the long-term assessment of vitrified RW properties. The materials of these studies can only indicate the degradation processes trend.

Data available on the analogues can be used straightaway to identify the processes occurring in various repository EBS materials, as well as those taking place at the barrier/barrier interface. One can also identify aggressive environments and unfavorable conditions under which corrosion and degradation processes may proceed more intensively. The studies considered and their findings demonstrate that numerous historical cements remain quite stable after hundreds and thousands of years. However, it should be emphasized that due to a different chemical composition, it seems risky to consider them as analogues in the long-term assessments of EBS material properties when it comes to materials based on Portland cement: these can only indicate the process trend. Data on archaeological analogues mostly provide some practical information about the degradation rate of the components constituting to the multi-barrier safety system of a repository. Archaeological artifacts being hundreds or thousands of years old often remain in very good condition. This may bolster confidence in the effectiveness of the designed EBS system and provide useful qualitative and, in some cases, quantitative indicators regarding their material properties that can be further used for modeling purposes and in the RW disposal safety assessments.

Table 2. EBS material analogues and summary of their properties

EBS material	Natural and historical analogues	Corrosion rate, μm/year	Discussion	Conclusion on the analogue applicability
Glass waste form	Volcanic glass	$N01 \cdot 10^{-6}$	Material is not stable	Due to different chemical composition and absence of radiation exposure, it can be used as an analogue indicating the development trend for the processes
	Uranium-containing glass	$N \cdot 10^{-2}$—$N \cdot 100$	Subject only to some slight alterations	
	Archeological glass (Northern Black Sea Region)		Subject only to some slight alterations	
	Roman glass		Subject only to some slight alterations	
Copper and copper alloys	Archeological finds (weapons and their parts, etc.)	$N \cdot 10^{-2}$—$N \cdot 100$	May stay stable and resist corrosion for quite long-time periods	Can be considered reliable analogues in the long-term assessment of copper properties, when copper is used in EBS construction
	Water supply systems		Material stays stable in reducing environment, but corrodes under aerobic conditions	
Iron and iron alloys	Anthropogenic artifacts (iron nails, weapons and their parts, etc.)	$N \cdot 10^{-2}$—$N \cdot 100$ (under reducing conditions) $N \cdot 10^{2}$ (under oxidizing conditions)	Material is stable under reducing conditions, degrades under aerobic conditions. Is still characterized with high-level strength and stability	Can be seen as a reliable analogue in the long-term assessment of container materials based on carbon steel
Cements	Natural cement from Jordan	–	Robust material with a long service life, the oldest cements are about 2 million years old.	Is a stable material, however, due to different chemical composition may be considered as an analogue indicating the development trend for the processes.
	Roman walls		Preserve their integrity for over 2,000 years	
	Cement solution from Hadrian's Wall		Is still characterized with high-level strength and stability	

Conclusions

The paper overviews the studies focused on natural and historical analogues of barrier materials aiming to provide long-term forecasts regarding their properties.

Such studies of natural and historical analogues and their findings can be used not only to predict the service life of safety barrier materials, but also to select the best natural conditions at the repository siting stage.

The accumulated knowledge about iron, copper and silicate glass behavior in analogue facilities provides a reliable basis for unbiased EBS material characterization. Based on data available on the corrosion rate in natural copper, iron (as an analogue of carbon steel) analogues or analogues of their alloys, degradation rates found for building and waste form materials (cement, concrete, glass) can be extrapolated for many years ahead, based on which one may select an optimal structure of the EBS cascade constituting to a multi-barrier disposal system.

The use of natural and historical analogues may help in:

- identifying the evolution trend of processes occurring within the repository EBS;
- assessing the properties of products generated due to EBS material degradation and those of newly formed barriers (for example, a layer of corrosion products deposited on the surface of corroding carbon steel or a layer of aluminosilicates on the corroding glass surface);
- developing plans for laboratory experiments and researches at analogous facilities and in URL;
- forecasting the service life of EBS systems.

Thus, the study of natural and historical analogues is believed a quite useful tool that can be applied to forecast repository evolution. However, the findings of such studies can be applied only if proper consideration is made of several other factors: firstly, the properties and chemical composition of RW, specific materials and methods involved in the construction of underground structures, geological conditions in the siting area.

Acknowledgments

The work was partially funded by the Ministry of Education and Science of the Russian Federation for the State Task of IGEM RAS

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Bibliographic description

Boldyrev K. A., Sobolev D. A., Kochkin B. T., Barinov A. S. Studies of natural and historical analogues and the use of their findings in the assessment of safety barrierbehavior under the safety demonstration of radioactive waste disposal facilities. *Radioactive Waste,* 2022, no. 3 (20), pp. 72—96. DOI: 10.25283/2587-9707-2022-3-72-96. (In Russian).